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**LEAD-FREE SOLDER**

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LEAD-FREE SOLDER

[Muen handa]

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[There are no amendments in this invention.]

Claims

1. Lead-free solder alloy that consists of 0.1-10 wt% Bi, 0.1-5 wt% Ag, 0.05-2 wt% Cu, 0.0005-0.1 wt% Ni, and 0.0005-0.01 wt% P, and the rest being Sn.
2. The lead-free solder alloy described in Claim 1, in which 0.01-0.5 wt% of In is also added.
3. Cream solder that contains the lead-free solder alloy in powder form described in Claim 1 or 2.
4. Molded solder that uses the lead-free solder alloy described in Claim 1 or 2.
5. Resin-containing solder that uses the lead-free solder alloy described in Claim 1 or 2.
6. Substrate that uses the lead-free solder alloy described in Claim 1.

7. Electronic product that uses the lead-free solder alloy described in Claim 1.

Detailed explanation of the invention

[0001]

Technical field of the invention

The present invention concerns lead-free solder alloy.

[0002]

Prior art

Soldering conventionally has used alloys that have Sn (tin) as the base, or a mixture of Sn+Bi (bismuth) as the base, to which Pb (lead) is added. Pb in the alloy functions to lower the fusion point of Sn at 232°C, and an alloy that is mixed together with 37 wt% Pb forms eutectic solder with a fusion point of 183°C, and it has been widely used for its proper fusion point. In this manner, Pb has been an inevitable component in the composition of solder alloys.

[0003]

However, Pb is a harmful element to humans and animals, and it is clear that solders that include Pb that are disposed of have the Pb component elute out gradually by acid rain, etc., which results in serious environmental contamination, such as penetration into the groundwater, etc. To respond to such a worldwide request for preventing environmental contamination by Pb, the research for lead-free solders has advanced primarily in the solder industry, and many techniques already have been disclosed. In these techniques, as a substitute for the function of Pb, silver (Ag), bismuth (Bi), antimony (Sb), zinc (Zn), cadmium (Cd), copper (Cu), magnesium (Mg), nickel (Ni), titanium (Ti), and indium (Ti [sic]), for example, are used in combination. However, some of these elements are still harmful and quite expensive as well. Moreover, they also do not necessarily substitute sufficiently for the function carried out by Pb.

[0004]

Problems to be solved by the invention

The purpose of this invention is to offer a lead-free solder alloy that does not contain Pb but maintains the character possessed by a Pb containing solder alloy as much as possible that has an excellent heat fatigue resistance character in particular.

[0005]

#### Means to solve the problem

For solving the aforementioned problem, the lead-free solder in this invention has the characteristic, in which its components consist of 0.1-10 wt% of Bi, 0.1-5 wt% of Ag, 0.05-2 wt% of Cu, 0.0005-0.1 wt% of Ni, and 0.0005-0.01 wt% of P, and the rest with Sn. Furthermore, this invention also concerns a solder alloy that has 0.01-0.5 wt% of In added to the aforementioned composition. This invention also includes cream solder that contains the aforementioned solder alloy as a powder, molded solder that uses the aforementioned solder alloy, and resin containing solder that uses the aforementioned solder alloy.

[0006]

By employing the aforementioned structure the solder in this invention can display an excellent character without containing harmful Pb at all. The contributions of the respective structural elements to the solder character will be explained below. Sn is the main component of the solder alloy. It is not toxic, has a characteristic of having an excellent wettability to the bonding base material, and it is a component that is inevitable as the solder base material. The mechanical characteristics can be improved, and the fusion can be lowered by adding Ag to Sn. The mixing amount of Ag in the solder alloy is 0.1-5wt%, ideally at 0.7-3 wt%. That effect is insufficient when it is less than 0.1 wt%. The fusion temperature becomes high when it exceeds 5 wt%, and it is also disadvantageous from the aspect of the cost.

[0007]

By adding Bi to Sn that has Ag added, the mechanical strength improves, and the fusion temperature can be lowered. The mixing amount of Bi is 0.1-10 wt%, desirably at 0.5-5 wt%. That effect is insufficient when the mixing amount of Bi is lower than 0.1 wt%. The mechanical strength improves when it is higher than 10 wt%, but the mechanical stretch dramatically decreases, which results in frequent occurrences of the heat fatigue. By furthermore adding Cu to Sn that already has Ag and Bi added together, the mechanical strength and the fatigue strength resistance can be improved. Cu is added at 0.05-2 wt% in the mixture. That effect is small when it is less than 0.05 wt%, and the fusion temperature increases when it is more than 2 wt%, and it cannot be used under the conventional conditions for use, or it can extend thermal damage to parts that are mounted over the substrate.

## [0008]

A characteristic of this invention is the manifestation of an excellent effect by a mixture of P and Ni in particular. P can improve the heat fatigue resistance characteristic and the mechanical characteristic of the solder (strength and stretch). Moreover, these characters will be dramatically improved as the mixing amount of P increases. The mixing amount of P is 0.0005-0.01 wt%. When the mixing amount is less than 0.0005 wt%, that effect does not exist. When exceeding 0.01 wt%, the mechanical strength will be improved, but the surface tension of the solder that is fused becomes great, and the issue of moisture in the atmosphere occurs. It also has been identified that the characteristic of heat fatigue resistance improves more by adding Ni. That effect becomes more apparent when mixing Ni together with P. The mixing amount of Ni is 0.0005-0.1 wt%. When it is less than 0.0005 wt%, there is no effect. When it is higher than 0.1 wt%, the improvement of the heat fatigue resistance will be reduced. In also improves the heat fatigue resistance characteristic and the mechanical characteristic. These characteristics will be improved without deteriorating other characters by adding In. The mixing amount of In is 0.01-0.5 wt% in the solder composition, desirably at 0.01-0.3 wt%. That effect is not displayed when it is less than 0.01 wt%, and it is not desirable when it is more than 0.5 wt% because the formation of oxides increases. This invention can offer a lead-free solder that has a better heat fatigue characteristic than in the conventional Sn-Ag, Sn-Zn, and Sn-Sb type lead-free solders by establishing Sn, Ag, Bi, Cu, Ni, and P in the aforementioned range.

## [0009]

A general solder manufacturing method may be used for obtaining a solder alloy from the composition of metallic materials in this invention. For obtaining a cream solder that contains the solder alloy in this invention, it can be obtained by pulverizing a solder alloy into a powder solder as is generally done, and uniformly mixing and kneading this together with a proper resin, such as rosin, for example, and with a flux that has a solvent, such as glycols and polyatomic alcohols, for example, as the main component and also contains additives, such as an activator, viscosity adjusting agent, and an antioxidant, for example, by a usual method. It can be prepared by a general method that is publicly known in the field of molded solders and resin containing solders.

[0010]

### Application examples

#### Application Examples 1-4

Each of the metallic materials in the compositions contained in Table 1 is fused at 400°C for 20 min into a uniform alloy (if possible, a concrete representative solder alloy manufacturing method should be described including the fusion container and the system, etc.).

Employing the evaluation method described below, the pull strength, stretch, wettability (wetting time and wetting stress), and the heat fatigue resistance characteristics of the obtained alloy are evaluated. Tables 1 and 2 show the results.

[0011]

#### Comparative Examples 1-6

The solders in Comparative Examples 1-6 are prepared in the compositions described in Table 1. The characters of the solders in Comparative Examples 1-6 are also evaluated in the same way as in the application examples, and Tables 1 and 2 show the results.

[0012]

Table 1

	はんだ合金組成(重量%)									溶融 温度	引張	
	S n	B i	A g	C u	N i	P	I n	S b	Z n		強度	伸び
実施例1 残部	5	2	0.5	0.005	0.001	—	—	—	—	8.35	18.3	
実施例2 残部	5	2	0.5	0.005	0.003	—	—	—	—	200	8.60	19.6
実施例3 残部	5	2	0.5	0.005	0.01	—	—	—	—	-217	8.78	23.9
実施例4 残部	5	2	0.5	0.005	0.003	0.2	—	—	—		8.98	24.2
比較例1 残部	5	2	0.5	—	—	—	—	—	—		8.21	16.8
比較例2 残部	5	2	0.5	—	0.003	—	—	—	—	200	8.30	18.6
比較例3 残部	5	2	0.5	0.005	—	—	—	—	—	-217	8.26	16.1
比較例4 残部	—	3.5	—	—	—	—	—	—	—	221	4.52	24.4
比較例5 残部	—	—	—	—	—	—	—	—	9	198	4.58	12.2
比較例6 残部	—	—	—	—	—	—	—	5	—	240	3.00	30.0

- Keys:
- 1 Composition of the solder alloy (weight%)
  - 2 Fusion temperature
  - 3 Pull
  - 4 Strength
  - 5 Stretch
  - 6 Application Example \_\_\_\_\_
  - 7 Comparison Example \_\_\_\_\_

## 8 The rest

[0013]

Table 2

サイクル数	200	250	300	350	400	450	500
実施例1	0	1.4	7.1	11.4	17.1	20.0	28.6
実施例2	0	0	0	2.9	4.3	4.3	4.3
実施例3	0	0	0	0	2.9	4.3	4.3
実施例4	0	0	0	0	4.3	5.7	5.7
比較例1	0	1.4	7.1	11.4	17.1	20.1	28.6
比較例2	0	0	4.3	12.9	15.7	21.4	21.4
比較例3	0	0	2.9	5.7	10.0	12.9	15.7
比較例4	0	1.4	8.5	14.3	21.4	27.1	32.9
比較例5	0	1.4	5.7	8.6	12.9	17.1	21.4
比較例6	0	2.9	10.0	15.7	22.9	31.4	34.3

- Keys:
- 1 Cycle number
  - 2 Application Example \_\_\_\_\_
  - 3 Comparative Example \_\_\_\_\_

[0014]

Evaluation method of the solder alloy

Pull strength and the stretch [at breaking]:

The solder alloy is held at 400°C, poured into a black lead mold that is heated to 270°C, cooled at 6°C/second, and a pull test piece in the shape indicated in Figure 1 is obtained. This test piece is provided to a pull test at the normal temperature at a pull speed of 5 mm/minute, and the stretch at breaking and the strength are obtained.

Wet character (for copper): The wet time and wet stress at 230-270°C are evaluated by the meniscus graph method.

Wet time: (About the evaluation method of the wet time and the judgment standards)

Wet stress: (About the evaluation method of the wet stress and the judgment standards)

[0015]

Heat fatigue characteristic

The solder alloy is soldered at 250°C by 8 connectors with 8 pins over a paper phenol substrate (back face: copper foil) of 100 mm x 100 mm x 1.8 mm. Figure 2 shows this mounting manner. This sample is provided to a heat impact test in 1 cycle of +80°C (30 minutes)--40°C (30 minutes), and the number of pins that form cracks per each 50

cycles up to 500 cycles is examined. The next equation indicates the crack occurrence rate.

$$\text{(Crack occurrence rate)} = (\text{The number of pins that form cracks}) / (\text{Total number of pins})$$

[0016]

#### Effect of the invention

The lead-free solder alloy of this invention does not contain lead at all and has excellent heat fatigue resistance as well as a satisfactory soldering performance.

#### Brief description of the figures

Figure 1 shows top view and side view diagrams that show the shapes of the test piece for the evaluation of the pull character of the solder.

Figure 2 is a cross-sectional diagram that shows the mounting of the test piece for the evaluation of the heat impact test of the solder.

#### Explanation of the reference symbols

1: Solder, 2: Land part (copper foil), 3: Phenol resin substrate, 4: Connector resin, and 5: Pin

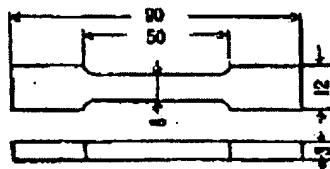


Figure 1

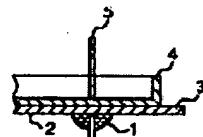


Figure 2